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METHOD FOR RECOVERING THALLIUM FROM THALLIUM-CONTAINING GLASS SCRAP

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Detailed description of the invention

[0001]

Technical field

The present invention is a method for recovering thallium from glass (general optical use) scrap that contains thallium.

[0002]

Prior art

Thallium has been used in recent years as a constituent of optical glass, and demand is increasing. Meanwhile, trace amounts of thallium can be found in lead and zinc ores and metallic thallium has been manufactured in the past by concentrating thallium from these refined ores or from precipitate products of thereof (e.g., see Japanese Patent Nos. 2,970,095 and 2,682,733). However, there are no reported examples of recovering thallium from glass (general optical use) scraps that contain thallium.

[0003]

Problem to be solved

The refined dusts of lead and zinc ores that contain thallium and their precipitate products normally have a fine grain size of 100 μm or less, and the thallium constituents contained therein are oxides or sulfides and can be easily extracted and recovered using an inorganic acid such as sulfuric acid, etc. However, the constituents of optical glass are SiO_2-MO-M_2O-M_2O_2-... (wherein, M is Tl, Li, Na, K, B, etc.), and optical glass is a material that is melted and then quench-solidified and used in the fabrication of small-aperture lenses and fibers. These fabrication processes produce scrap in the form of fabrication ends from 50 mm-diameter blocks and 1 mm-diameter rods, several mm-diameter and smaller pulverized glass scrap. Unless an economical method is developed for recovering thallium from this glass scrap, the thallium will be discarded without being recovered.

[0004]

This is because the recovery of thallium melted into the glass material is considered to be difficult. The invention in this application is an industrially viable method to recover thallium that overcomes these considerations.

[0005]

Means to solve the problem

This invention is a method of recovering thallium from thallium-containing glass scrap, wherein glass scrap containing thallium is pulverized to a grain size of 300 μm or less, the resulting glass scrap is extraction treated with an inorganic acid to bring the thallium constituent out of solution and, as necessary to precipitate and remove metal inclusions from the extraction solution, the metallic thallium is precipitated out by adding a metal more noble than thallium to the extraction solution.

[0006]

Conditions of embodiment

The glass scrap and pulverized scrap generated in the process of manufacturing lenses from high-refractive index optical glass, and the fabrication ends of glass rods and pulverized scrap generated in the process of manufacturing high-refractive index glass fiber are used as the thallium-containing glass scrap in the method of this invention. Strong sulfuric acid, sulfuric acid, nitric acid, and hydrochloric acid are used as the inorganic acid, but sulfuric acid is preferred because of its handling properties and economy. Metallic aluminum, metallic zinc, and metallic iron are used in plate, granular, or powdered form as the metal that is baser than thallium, and since a fine oxide skin forms on the surface of the aluminum metal, slowing its reaction speed, while the divalent ions produced after reaction in metallic iron are oxidized by the air in the atmosphere to trivalent ions, causing iron hydroxide to precipitate and contaminate the metallic thallium, it is simplest to use zinc.

[0007]

In the implementation of this invention, the glass scrap is pulverized to a grain size of 300 μm or less by a compression-type crusher, such as a jaw or cone crusher, an impact compression-type grinder, such as a ball mill, or an abrasive pulverizer, such as a roller mill. 20 mm glass scrap is coarsely crushed by a jaw crusher or the like, and then finely pulverized by a ball mill, etc., but it is adequate if the largest grain size is 300 μm or less, with an average grain size of 150 μm. Large grains of 300 μm or greater dramatically reduce the thallium extraction speed, while grains of less than 70 μm will not yield extraction results proportionate to the energy consumed.

[0008]

When extraction treating the glass scrap with an inorganic acid, 2 to 5 moles of the inorganic acid, if it is a monobasic acid, or 1 to 2.5 moles, if it is a dibasic acid, are added per

1 mole of thallium content in the glass scrap, which has been pulverized to 300 μm or less. When adding the inorganic acid, it is preferable to add water and make a slurry of the glass scrap and gradually add the inorganic acid to maintain a pH of 1 to 2, as this will minimize dissolution of the SiO_2 constituent, which makes it difficult to filter insoluble solids from the extraction solution.

[0009]

The extraction treatment causes the thallium contained in the glass scrap to react with the inorganic acid and to dissolve as a salt of the inorganic acid. For example, when sulfuric acid is used, the reaction is as shown in the formula below.

$$Tl_2O + H_2SO_4 \rightarrow Tl_2SO_4 + H_2O$$

Extraction by inorganic acid is performed for 1 h or more at a temperature of 40°C or higher, while stirring. When performed using 95% sulfuric acid, around 2 h at 40 to 60°C is suitable. After extraction, the extraction solution and insoluble solids are separated. Conventional methods may be employed to separate the insoluble solid precipitate. When separation is done, the purity of the thallium can be increased by adding a precipitant, such as soda sulfide, to precipitate and remove metal inclusions, such as copper, lead, cadmium, etc.

[0010]

Next, a metal more noble than thallium is added to the resulting extraction solution. For example, a plate of metal that is more noble than thallium is immersed in the extraction solution, causing thallium to precipitate onto the surface of the metal plate, then the precipitated thallium is scraped off. The amount of the more noble metal added is preferably 1/2 mole for zinc, 1/3 mole for aluminum, or 1/2 mole for iron per 1 mole thallium content in the extraction solution. When using a granular or powdered base metal, it is especially preferable that less than the chemical equivalent be added since, if more than the equivalent is added, the excess metal will form residue on the precipitated thallium, contaminating the recovered metallic thallium. When the base metal is used in plate form, it is possible to precipitate as little as 100 mg/L of residual thallium in the extraction solution without contaminating the precipitated thallium. The resulting thallium is in porous or powdered form and can be compressed as desired into tablets.

[0011]

The resulting metallic thallium can be melted down or further refined, as required, and then melted and cast. For example, after rinsing precipitated porous thallium with water, it can be pressed into tablets, melted together with solid caustic soda as flux, and cast as high-purity thallium.

[0012]

This invention will be described in detail below using application examples, but this does not limit the scope of this invention to these examples.

[0013]

Application examples

Application Example 1

(1) Pulverization

The glass block (50 mm x 100 mm L) remaining after cutting out the raw material for a high-refractive index optical glass lens was crushed to 30 mm or smaller scrap by a jaw crusher, and then pulverized for 3 h in a ball mill using an alumina ball, and sifted through a 250 μm aperture sieve to yield glass powder with a grain size of 250 μm or less. This glass powder had the following composition.

Constituents (wt%): $SiO2_2$ (35), Tl_2O (40), B_2O_3 (10), Na_2O (10)

[0014]

(2) Extraction

20 L of water were mixed with 2000 g of the resulting glass powder to make a slurry, and then 920 g of 98% concentrated sulfuric acid were gradually added while maintaining a pH of 1 to 2, and stirred for 3 h at 50°C. 1324 g (840 g dry weight) of solids were then filtered out to yield 21 L of extraction solution. The composition of the extraction solution was as shown below, wherein 95.5% of the thallium in the glass scrap had been separated.

Extraction solution constituents (g/L)

Constituents (g/L): Tl (35), Na (11), B (3.5), Cu (0.0003), Fe (0.002), Pb (0.0005)

[0015]

(3) Precipitation

Four 100 mm x 50 mm x 5 mm-thick pure zinc plates were immersed into 21 L of the extraction solution and slowly stirred for 2 h at 50°C. The thallium in the extraction solution aggregated out onto the surface of the zinc plates as metallic thallium. The precipitated metallic thallium was then stripped off the zinc plates and, after rinsing with pure sulfuric acid and water, the water was squeezed out and it was formed into 30 mm-diameter x 20 mm-thick tablets. 750 g of the molded metallic thallium and 350 g of solid caustic soda were placed together in a graphite crucible and heated for 2 h at 400°C, and the molten thallium was poured into iron molds and cast to yield 715 g of 99.9% pure metallic thallium.

[0016]

Application Example 2

(1) Pulverization

1500 g of ground glass scrap produced in the process of manufacturing high-refractive index optical glass fiber were used for extraction. The grain size distribution (wt%) in the ground glass scrap powder was as follows.

>300 μm (3), 300-150 μm (5), 150-100 mm (10), <100 μm (82)

In addition, the composition of the ground glass scrap powder was as follows.

Constituents (wt%): SiO_2 (45), Tl_2O (39), B_2O_3 (5), Na_2O (5), PbO (0.014), Cu_2O (0.02)

[0017]

(2) Extraction

15 L of water were added to the 1500 g of ground glass scrap powder to make a suspension, and then 470 g of 95% sulfuric acid were added and stirred for 3 h at 50°C. Since the extraction solution contained 15 mg/L copper, 200 g of soda sulfide were added to precipitate the copper as copper sulfide. 1000 g (650 g dry weight) of solids were then filtered out to yield 15 L of extraction solution. The composition of the extraction solution was as follows, wherein 95.5% of the thallium in the glass scrap had been separated.

Extraction solution composition (g/liter)

Constituents (g/L): Tl (35), Na (3), B (1.5), Cu (0.0001), Pb (0.0005)

(3) Precipitation

The 15 L of extraction solution were processed in the same manner as disclosed in (3) Precipitation of Application Example 1 to yield 510 g of 99.9% pure metallic thallium.

[0018]

Application Example 3

108 g of 98% pure metallic zinc powder (0.95 equivalents to thallium) were added to 20 L of extraction solution obtained by the same process as in Application Example 1 and stirred for 2 h at 50°C. 650 g (dry weight) of sponge thallium aggregated into a 30 mm clump was recovered from the thallium in the solution. 3 g/L of thallium remained dissolved in the processed solution. The recovered sponge thallium was rinsed and molded in the same manner as in Application Example 1, and then melted to yield 620 g of 99.9% pure metallic thallium.

[0019]

Effect

With this invention, thallium can be efficiently recovered from thallium-containing glass scrap.